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LIQUID MIXTURES OF TELLURIUM AND SODIUM TELLURIDE

I. Specific Resistance as a Function of Composition and Temperature

by

STANLEY W. GLASS

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A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE DEPARTMENT OF BROWN UNIVERSITY, 1929

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LIQUID MIXTURES OF TELLURIUM AND SODIUM TELLURIDE
I. SPECIFIC RESISTANCE AS A FUNCTION OF COMPOSITION AND TEMPERATURE

BY STANLEY W. GLASS

The present investigation was originally undertaken for the purpose of studying the conductance of liquid mixtures of tellurium and sodium telluride. According to Pellini and Quercigh[1] sodium and tellurium are completely miscible in the liquid state with the exception of an interval lying between 25 and 37 atom per cent. of sodium. Their diagram indicates the existence of a normal telluride, Na_2Te, which is quite stable, melting at approximately 1000°, as well as two higher tellurides, to which they assign the formulae Na_3Te_2 and Na_2Te_7. The gap in the solubility diagram occurs in the region corresponding to the composition Na_2Te_7. In carrying out conductivity measurements on various liquid mixtures, the appearance of new phases was indicated by inflection points in the resistance temperature curves. These points did not agree with the earlier data of Pellini and Quercigh and, accordingly, the phase diagram of mixtures of tellurium and sodium telluride was redetermined by the method of thermal analysis. The results of conductance measurements will be presented first since they will later be of assistance in interpreting the phase diagram.

Materials

Tellurium was purified according to the following procedure. The commercial metal was dissolved in dilute nitric acid and the basic nitrate formed was allowed to settle. The supernatant liquid was decanted and evaporated to dryness. The residue so obtained, together with the basic nitrate originally precipitated, was decomposed by heat. This impure oxide was dissolved in hydrochloric acid, and the resulting solution was evaporated to dryness in order to expel traces of nitric acid. The residue was now dissolved in concentrated hydrochloric acid, diluted with an equal volume of water, made slightly alkaline with ammonium hydroxide, and then acidified with dilute acetic acid. The tellurium dioxide precipitated in this process was thrown on a filter, washed and dried. It was then heated to about 600° in a Pyrex tube through which a slow stream of oxygen was passed. This served to remove most of the volatile impurities consisting chiefly of selenium dioxide. The residue was again dissolved in concentrated hydrochloric acid and the solution was saturated in the cold with sulphur dioxide.[2] Selenium was precipitated[3] and separated by filtration through asbestos. The filtrate was

[1] Atti Acad. Lincei, (5), 19 II, 350 (1910).
[2] Lenher and Kao: J. Am. Chem. Soc., 47, 769 (1925).
[3] Keller: J. Am. Chem. Soc., 19, 773 (1897).

diluted to about 6N and again saturated in the cold with sulphur dioxide in order to precipitate the tellurium. The precipitated metal was filtered and thoroughly washed with water and, finally, with alcohol and dried quickly at 110°C. The metal was then distilled in vacuo in an electric furnace. The purified product gave no evidence of impurities when subjected to a spectroscopic test.[1]

Sodium telluride was prepared by treating a weighed quantity of freshly-cut sodium in liquid ammonia with finely divided metallic tellurium. The metal was added slowly until the blue color, due to free sodium, just disappeared. Sodium telluride Na_2Te is only slightly soluble in liquid ammonia, the saturated solution being colored light yellow. The ditelluride, Na_2Te_2, is readily soluble and yields a highly colored violet-blue solution. The characteristic color effects make it possible to adjust the composition of the product accurately to the formula Na_2Te and the total weight of material is determined from the amount of tellurium added, thus making it unnecessary to weigh the sodium.

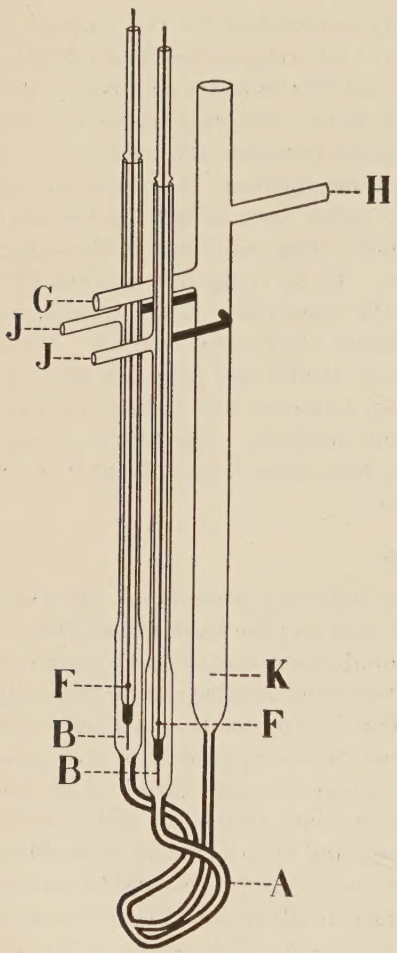

FIG. 1
Cell used in measuring Resistance of Mixtures of Te and Na_2Te

The reaction between sodium and tellurium is carried out in a closed tube cooled to liquid ammonia temperatures by means of a bath of boiling ammonia. When the reaction is completed, the ammonia is allowed to evaporate and the necessary quantity of tellurium is added in order to produce an alloy of any desired composition. The tube containing the sodium telluride and tellurium is then heated in an atmosphere of ammonia or nitrogen to a temperature of about 600° and the contents are thoroughly stirred. After allowing the tube to cool, it may be broken and the contents transferred to the measuring apparatus in an atmosphere of nitrogen.

Apparatus and Procedure

Thermostat. The thermostat employed in this investigation was similar to that previously described by Kraus and Johnson,[2] and further description may, therefore, be omitted.

[1] Dudley and Jones: J. Am. Chem. Soc., **34**, 1004 (1912).
[2] Kraus and Johnson: J. Phys. Chem., **32**, 1281 (1928).

The Conductivity Cell. In the preliminary measurements, a Pyrex glass cell was employed, similar in construction to the high-resistance cells used by Kraus and Johnson in measuring the resistance of metallic tellurium. It was found, however, that mixtures of sodium telluride and tellurium slowly react with glass so that reproducible results cannot be obtained. Accordingly, a similar cell was constructed of clear fused quartz. The general arrangement of the cell is shown in Fig. 1. The capillary A of this cell had a length of approximately 30 cm. and an internal diameter of 1.5 mm. The electrodes BB, making contact with the melt, were platinized. The process of platinization had to be repeated after each series of measurements, as otherwise, satisfactory results could not be obtained. Copper leads were hard soldered to the platinum electrodes at FF, the junctions being located below the level of the thermostatic liquid in order to avoid thermoelectric effects.

In all, five cells of the type described were employed. Their resistance constants were determined at 25°C by means of a normal solution of potassium chloride made up by weight according to directions of Kraus and Parker.[1] The specific conductance of 1.0 N potassium chloride solution was assumed to be 0.11180. The data relating to the calibrations are summarized in Table I.

TABLE I

Constants of Conductivity Cells

Cell	1	2	3	4	5
Resistance	7248.4	7179.0	7171.0	7161.4	7106.5
Constant	810.4	802.6	801.7	800.6	794.5

Measuring Apparatus. The electrical resistance of alloys of higher specific resistance was measured by means of a drum-wound bridge and telephone. A Vreeland oscillator served as source of alternating current and the usual precautions were taken as to screening, grounding, etc. In the case of alloys, of lower resistance, a direct current with a precision Wheatstone bridge was employed. Polarization was marked in alloys of higher resistance.

The temperature was measured by means of a platinum platinum-rhodium thermocouple, which was calibrated against the boiling point of water and the melting points of standard samples of tin, lead, zinc and aluminum.

Procedure. The alloy, prepared as already described, was quickly transferred into tube K of the conductivity cell under an atmosphere of nitrogen. The cell was then exhausted and repeatedly washed with fresh nitrogen to remove traces of air. Finally, the cell was filled with nitrogen to a pressure approximately 1 cm. above that of the surrounding atmosphere, and this pressure difference was maintained throughout all subsequent operations. Tubes G, JJ and H served to make connection to the auxiliary apparatus as described by Kraus and Johnson.

The cell containing the alloy was introduced into the thermostat and heated to a temperature above 500°, or sufficiently high to completely melt

[1] Kraus and Parker: J. Am. Chem. Soc., 44, 2426 (1922).

the alloy. By introducing nitrogen through the tubes JJ and the capillary A, the liquid in tube K was stirred. It was then allowed to flow into the capillary making contact with the electrodes BB. The resistance was measured and the process of stirring repeated until constant values were obtained. The resistance was then measured at successively lower temperatures at intervals of from 10° to 25°. When the measurements were completed, the alloy was melted and blown out of the capillary into the tube K by means of nitrogen, after which the cell was removed from the thermostat and the alloy allowed to solidify.

Experimental Data

Composition of Alloys. In Table II are given the data relating to the composition of the various alloys used. Column 2 indicates where the resistance measurements are tabulated. Otherwise the table is self-explanatory. As explained above, the weight of sodium given in column 4 has been calculated from the equivalent weight of tellurium used in the neutralization of sodium, the weight of which is given in column 3. Analytical checks indicated that the composition of the alloys as calculated corresponded closely to the true values.

TABLE II

Data on Preparation of Alloys used in Conductance Measurements

Composition Atom % Na	Table No.	Wt. Te for Na_2Te in g.	Calc. wt. Na in g.	Total wt. Te in g.
54	III	12.042	4.3447	20.517
50	IV	11.179	4.0331	22.357
48	V	9.927	3.5816	21.509
46	VI	9.416	3.3971	22.107
44	VII	8.701	3.1392	22.156
40	VIII	9.293	3.3530	27.880
35	IX	6.403	2.3103	23.784
30	X	5.393	1.9459	25.171
25	XI	4.298	1.5507	25.778
20	XII	3.028	1.0924	24.223

TABLE III

Resistance of Alloy, $Na_{54}Te_{46}$, Cell No. 5

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
503.1	1.732	0.5774	456.0	0.4593	2.177
480.6	1.503	0.6654	436.2	0.2900	3.448
461.9	1.319	0.7580			

Results. The specific resistance of the various alloys at different temperatures are given in Tables III-XII. The composition of each alloy and the cell used are indicated at the head of the several tables. In Figs. 2, 3 and 4, the specific resistance is plotted as a function of the temperature for alloys corresponding to the compositions $Na_{50}Te_{50}$, $Na_{40}Te_{60}$ and $Na_{25}Te_{75}$ respectively. The curves for other compositions are similar to one or another of the three reproduced in the figures. In Fig. 5 values of the specific resistance are plotted as a function of the composition at different temperatures.

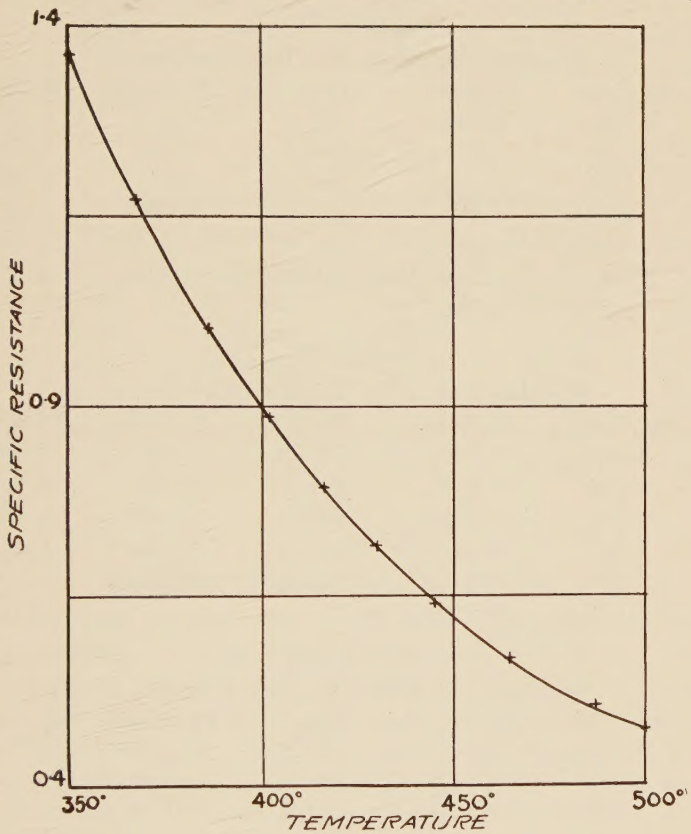

FIG. 2
Resistance Temperature Curve of Alloy $Na_{50}Te_{50}$.

TABLE IV

Resistance of Alloy, $Na_{50}Te_{50}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
500.4	2.106	0.4749	402.2	1.129	0.8858
487.6	1.977	0.5057	386.4	0.9966	1.0034
464.5	1.754	0.5701	367.4	0.8526	1.173
446.3	1.562	0.6402	350.2	0.7338	1.363
430.1	1.394	0.7173	328.6	0.1902	5.258
416.0	1.257	0.7957			

TABLE V

Resistance of Alloy, $Na_{48}Te_{52}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis	Temp.	Sp. Cond.	Sp. Resis
497.2	2.357	0.4243	399.4	1.312	0.7624
480.0	2.134	0.4690	381.1	1.159	0.8629
458.1	1.893	0.5282	358.6	0.9766	1.024
438.0	1.674	0.5975	324.8	0.4062	2.462
410.0	1.408	0.7100			

TABLE VI

Resistance of Alloy, $Na_{46}Te_{54}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
499.6	2.835	0.3527	382.5	1.318	0.7587
483.0	2.555	0.3914	363.2	1.143	0.8745
465.0	2.277	0.4391	349.0	1.011	0.9886
449.9	2.075	0.4819	335.5	0.9016	1.109
431.8	1.851	0.5403	323.9	0.8169	1.224
414.2	1.645	0.6079 Rose suddenly to		0.4404	2.271
396.9	1.457	0.6862			

TABLE VII

Resistance of Alloy, $Na_{44}Te_{56}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
499.3	3.501	0.2856	381.3	1.483	0.6745
475.3	2.930	0.3413	363.2	1.287	0.7772
456.1	2.584	0.3870	347.2	1.128	0.8863
440.7	2.330	0.4292	332.0	0.9841	1.016
419.9	1.992	0.5020	320.4	0.8801	1.136
402.0	1.737	0.5756			

TABLE VIII

Resistance of Alloy, $Na_{40}Te_{60}$, Cell No. 1

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
497.3	6.051	0.1653	350.8	1.586	0.6306
467.6	4.648	0.2151	340.9	1.676	0.5968
444.1	3.780	0.2646	334.2	1.626	0.6148
420.0	3.032	0.3298	320.2	1.515	0.6600
394.4	2.402	0.4164	311.3	1.434	0.6975
372.5	1.951	0.5125	297.9	1.000	0.9995
			Reheated and stirred		
354.0	1.630	0.6133	435.0	3.512	0.2847
333.1	1.614	0.6195	409.6	2.769	0.3612
325.2	1.557	0.6422	364.0	1.800	0.5556
319.0	1.500	0.6667	348.0	1.736	0.5761
Reheated and stirred					
426.1	3.253	0.3074	351.0	1.741	0.5743
392.8	2.378	0.4206	358.3	1.735	0.5764
365.3	1.826	0.5477	359.3	1.735	0.5763

TABLE IX

Resistance of Alloy, $Na_{35}Te_{65}$, Cell No. 4

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
511.3	16.08	0.06217	385.1	4.640	0.2155
487.2	12.55	0.07970	368.1	4.101	0.2438
468.0	10.23	0.09772	353.9	3.743	0.2672
452.6	8.658	0.1155	339.1	3.321	0.3011
436.0	7.197	0.1389	328.5	3.029	0.3302
428.5	6.613	0.1512	315.5	2.697	0.3707
414.2	5.618	0.1780	305.2	1.520	0.6580
400.0	4.969	0.2012			

TABLE X

Resistance of Alloy, $Na_{30}Te_{70}$, Cell No. 2

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
506.5	42.92	0.02330	371.4	9.226	0.1084
491.8	35.83	0.02891	356.6	7.848	0.1274
476.3	30.08	0.03324	348.0	7.178	0.1393
451.8	22.55	0.04434	336.9	6.316	0.1583
431.1	17.71	0.05645	323.6	5.419	0.1845
405.1	13.54	0.07385	313.7	4.788	0.2088
387.9	11.02	0.09077	302.9	2.831	0.3532

TABLE XI

Resistance of Alloy, $Na_{25}Te_{75}$, Cell No. 4

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
501.1	102.08	0.00980	364.8	14.76	0.06773
467.7	65.43	0.01528	354.6	12.90	0.07752
443.2	48.31	0.02070	339.5	10.66	0.09383
422.0	30.30	0.03300	324.1	8.710	0.1148
401.7	23.60	0.04236	310.8	7.286	0.1372
389.8	20.33	0.04918	304.9	6.701	0.1492
377.0	17.33	0.05772			

TABLE XII

Resistance of Alloy Na_{20} Te_{80}, Cell No. 3.

Temp.	Sp. Cond.	Sp. Resis.	Temp.	Sp. Cond.	Sp. Resis.
527.0	250.8	0.003986	374.9	27.59	0.03625
495.4	191.4	0.005225	356.7	22.87	0.04373
471.8	151.7	0.006592	332.0	17.76	0.05631
448.9	117.8	0.008487	315.9	15.04	0.06651
425.0	88.16	0.01134	301.0	12.88	0.07765
404.8	77.72	0.01287			

Discussion

In all cases, the specific resistance of the alloys diminishes markedly with increasing temperature, approximately, according to an exponential function. At higher concentrations of sodium, the resistance increases regularly with decreasing temperature without singularities until a large discontinuous increase of the resistance occurs. This latter change is doubtless due to the appearance of a solid phase. In general, at these higher concentrations of

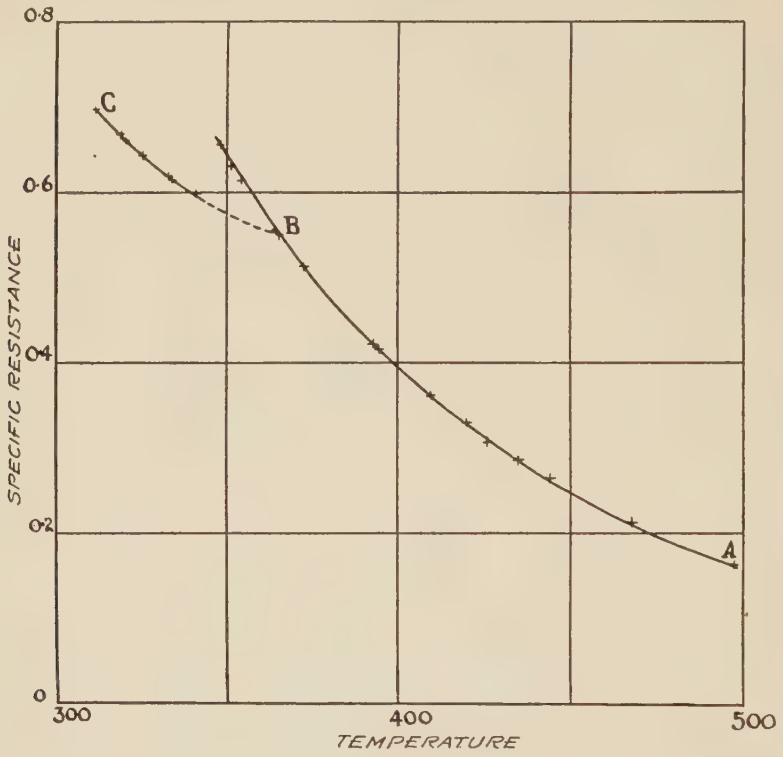

FIG. 3
Resistance Temperature Curve of Alloy $Na_{40}Te_{60}$.

sodium, there was no indication of the initial appearance of a solid phase at temperatures corresponding to the melting point diagram. Transformation was apparently suspended until, when crystalization set in, substantially complete solidification occurred. It may be noted that on investigating the melting point diagram in the same region by the method of thermal analysis consistent results could be obtained only under conditions of vigorous stirring and seeding of the melt. In the case of alloys richer in tellurium, the initial appearance of the solid phase in the neighborhood of the expected temperatures was readily determinable. Under these conditions, the resistance increased continuously with falling temperature until a solid phase began to appear, when the direction of the curve underwent a discontinuous change although the resistance itself varied continuously. This is well illustrated

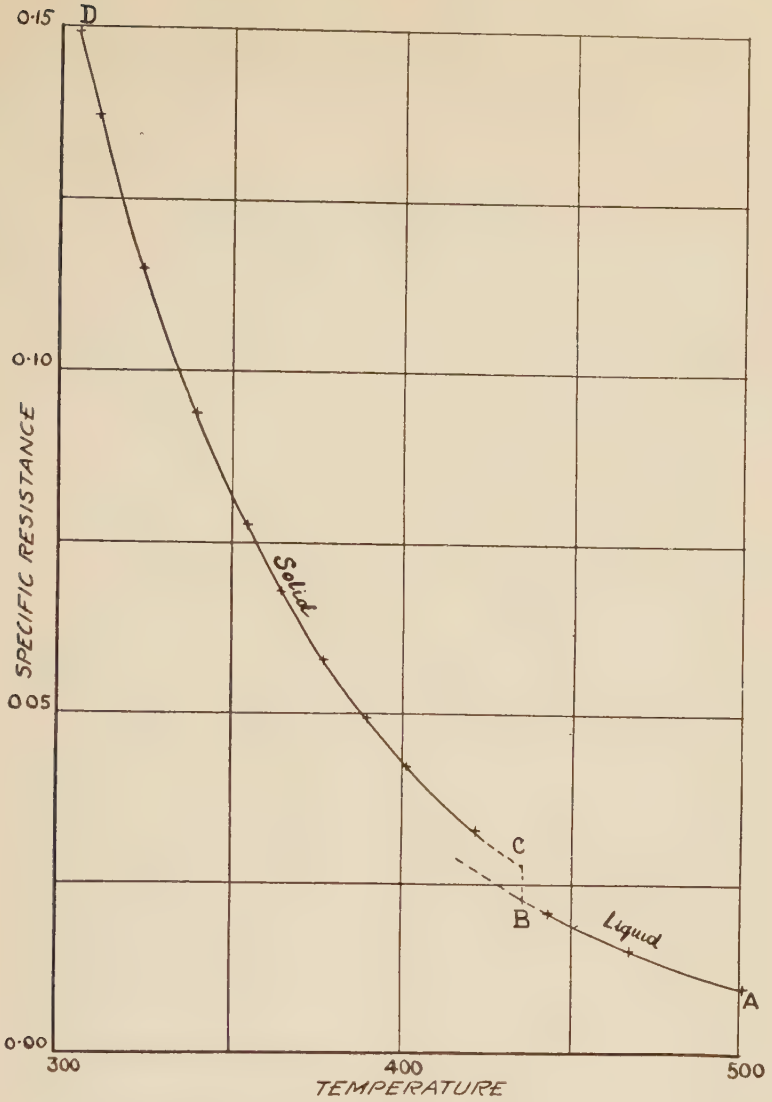

FIG. 4
Resistance Temperature Curve of Alloy $Na_{25}Te_{75}$.

in Fig. 3 with an alloy containing 40 atom per cent. of sodium. Three series of measurements were carried out which showed that the initial point of crystalization lies at approximately 365°. In this case, the liquid phase persisted some degrees into the metastable region, when a discontinuous change of resistance occurred. The temperature at which a solid phase should initially appear can be approximated by extrapolation of the curves to their point of intersection. The resistance of the mixture of liquid and solid is slightly lower than that of the homogeneous liquid at the same temperature. The curve BC relating to mixtures of liquid and solid lies below AB for the homo-

geneous liquid. Finally, at still lower temperatures, the eutectic between Na_2Te_6 and Na_2Te_2 is reached and complete solidification occurs with a discontinuous change in the resistance. It was not possible to obtain the exact temperature of the eutectic point by means of the resistance effect owing to suspended transformation. An alloy containing 35 atom % of sodium gave an inflection point at 405° and one containing 20 atom % at 430°.

The alloy containing 25 atom % of sodium showed a small discontinuous change of resistance at 436°. This corresponds to the congruent melting point of the compound Na_2Te_6. The curve AB of Fig. 4 relates to the homogeneous liquid alloy of the above composition, while the curve CD relates to the homogeneous solid alloy. It will be observed that the solid alloy is a fairly good electrical conductor. Both curves follow an exponential relation quite closely.

By means of the conductivity method, the following points were established on the melting point curve.

TABLE XIII

Initial Crystalization Temperature by Conductance Method

Atom % Sodium	20	25	35	40
Temp. of initial Cryst.	430	436	405	365

The resistance method is often advantageous in determining the temperature at which a solid phase begins to appear. The two branches of the resistance-temperature curve, relating respectively to the homogeneous liquid and to the mixture of liquid and solid, intersect and the point of intersection may be approximated fairly closely. Suspended transformation merely increases the extrapolation and thus increases the error but the result is definite. In regions where the method of thermal analysis breaks down because of suspended transformation, the conductivity method serves as a valuable supplement to the former. In a succeeding paper, the results, just presented, will be used in interpreting the phase diagram of the system Te-Na_2Te.

In Fig. 5, values of the resistance are plotted as a function of the composition at a series of temperatures.

As may be seen from this figure, the alloys containing higher percentages of tellurium are extremely good conductors. Without doubt, these alloys are true metals: that is, the current is carried by a process of metallic conduction. The metallic nature of these alloys, moreover, is borne out by their appearance, which is distinctly that of a metal. It will be noted that at 500°, the resistance-composition diagram has an inflection point indicating that, at higher concentrations of sodium telluride, the resistance approaches a definite maximum value. This probably means that as the composition of the alloys approaches that of the normal telluride, Na_2Te, the conductance is more and more largely due to an electrolytic process: for pure sodium telluride is a normal type of salt and, doubtless, conducts according to an electrolytic process. In general, the order of magnitude of the resistance of mixtures containing larger percentages of sodium telluride corresponds to that of fused

salts. As the temperature diminishes, the resistance of all the alloys increases markedly, but the curves are, in general, of much the same form.

There can be little doubt that in mixtures of sodium telluride and tellurium, we have an instance of mixed metallic and electrolytic conduction. The higher the percentage of tellurium, the more does the metallic overbalance the electrolytic process.

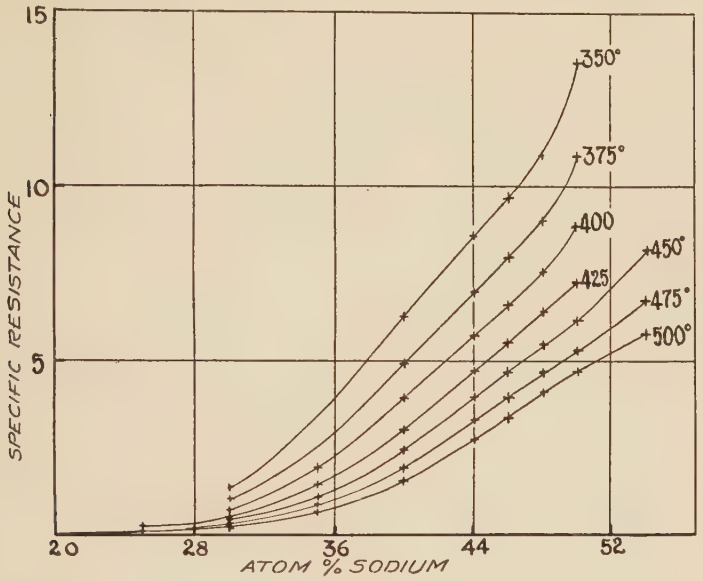

FIG. 5
Resistance of Alloys as a Function of Composition at Different Temperatures.

Summary

A method is described for preparing alloys of tellurium and sodium telluride of desired composition.

The resistance of liquid mixtures of tellurium and sodium telluride has been measured at various concentrations up to 54 atom % of sodium and at a series of temperatures up to 500°.

Mixtures rich in tellurium are good conductors and conduct metallicly. The conductance of mixtures rich in sodium telluride approximates that of fused salts and the conduction process is an electrolytic one.

Observations are recorded that indicate that sodium telluride and tellurium are completely miscible in the liquid state.

From the conductance-temperature curves, it may be inferred that sodium and tellurium form a compound, Na_2Te_6, having a congruent melting point at 436°.

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